



The Design, Synthesis, and Characterization of "Smart" Donor-Acceptor Biaryls

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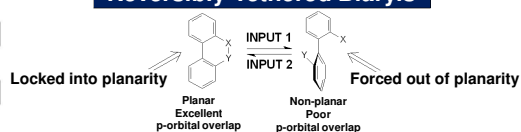


Mission

❖ To investigate the synthesis of tethered organic biaryl systems for ultimate application in sensing and molecular electronics.

❖ We aim to synthesize biaryls with a tether that can be reversibly opened and closed. Thus, these molecules can be "tethered" shut ($\theta=0^\circ$) or left "open" ($\theta \gg 0^\circ$), depending on external stimuli such as pH, thereby reversibly and controllably affecting their physical properties such as conductance and fluorescence.

Reversibly Tethered Biaryls



❖ The effect of the addition of different substituent groups, such as electron donating/accepting groups, will be studied.
❖ The molecules made during the project have broad application in the field of material science and the synthetic pathway represents a novel strategy for the synthesis of these biaryl lactones.

Background

Molecular Machine:

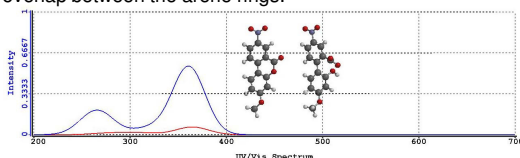
A functional molecular scale system designed to perform a large amplitude of directional mechanical motion as result of a *defined energy stimulus*.

Molecular Switch:

- Any chemical system that can exist in at least two forms having different spectral, electrochemical, or magnetic properties.
- Interconversion can only occur as a result of a defined energy stimulus.

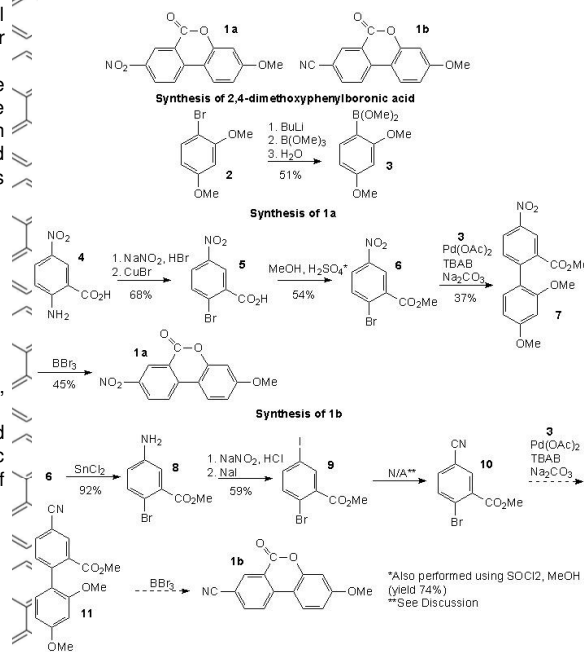
θ -Dependent Properties:

❖ Compounds that contain the biphenyl moiety (biaryls) are known to have drastically different properties depending on their equilibrium dihedral angles.
❖❖ For instance, it has long been known that both the UV-Vis spectra and fluorescent properties of biaryls are highly contingent on whether the biphenyl moiety can adopt a planar or near-planar configuration, thus allowing pi orbital overlap between the arene rings.

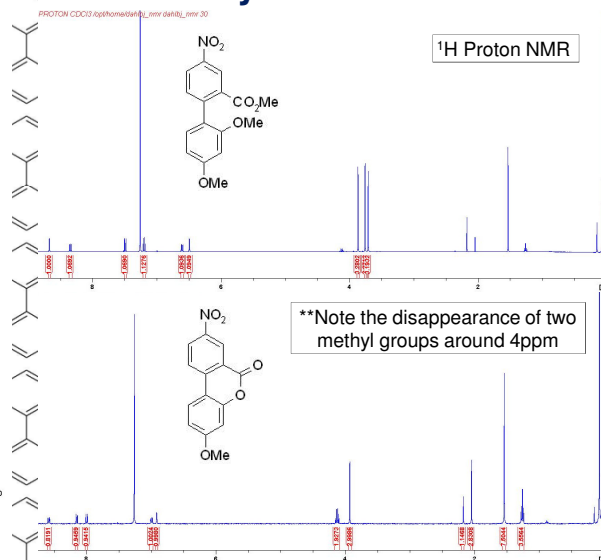


Calculated UV/Vis spectrum at B3LYP/6-31+G* level of theory on Spartan '08

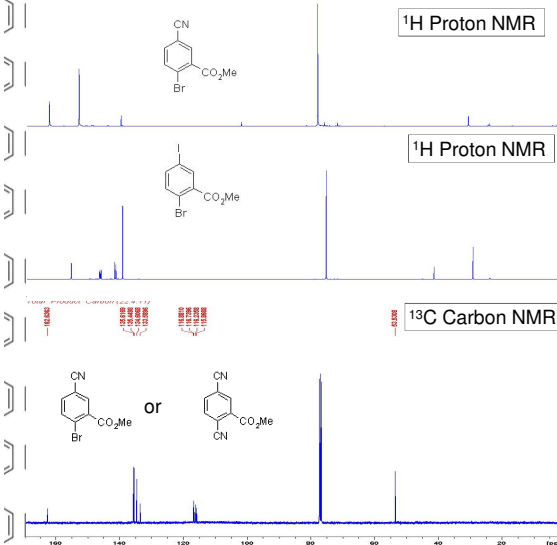
Proposed Synthetic Pathway



NMR Analysis of 1a



Spectral Analysis of 10



Multiple reactions have been utilized to cyanate **9** into the desired cyano compound, **10**. Thus far, all of our approaches have been microwave enhanced. The first reaction attempted was a Rosenmund-von Braun reaction, without the use of Pd catalyst. Upon reaction "failure", a Pd catalyst-dependent reaction was used with similar results. Upon closer structural/spectral investigation, it is thought that **10** was the major product of each reaction all along.

Future Projects

- ❖ The research proposed here is the first step in answering some fundamental questions about the design, synthesis and characterization of "smart" biaryls.
- ❖ To analyze how the ring-opened and closed states of 4,4'-dithiol substituted hybrid systems can effect electron transport properties of Au nanoparticle arrays functionalized with these ligands.
- ❖ This would aide in determining if the change in the electronic character of the molecules associated with ring-opening and closing could be useful in fabricated devices and to gain more fundamental insight into how ligand conformations in metal nanoparticle arrays affect electronic and/or photonic communication between the nanoparticles.

Acknowledgments

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